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High T_c superconductors have been investigated in both bulk and thin film form. Investigations have been carried out on the magnetic properties of both polycrystalline and single crystal forms of $YBa_2Cu_3O_7$ focussing on time-dependent effects. Single crystals of this material have been studied using scanning tunneling microscopy. Techniques for fabricating thin films have been developed. These include sputtering using spherical targets and co-evaporation using pure ozone as an oxidant. The latter permits the in-situ formation of films without any post-deposition annealing step. Superconducting fluctuations and the Kosterlize-Thouless transition have been studied in the Tl-Ba-Ca-Cu-O films.

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Scientific Report

HIGH TEMPERATURE SUPERCONDUCTING COMPOUNDS

GRANT NO. AFOSR-87-0372

31 March 1989

School of Physics and Astronomy
and
Department of Chemical Engineering and Materials Science
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I. INTRODUCTION

This report describes the results of research during the first eighteen months of AFOSR Grant No.87-0372 which is concerned with the subject of the anomalously high T_c superconducting compounds. These materials first attracted world-wide attention more than two years ago. The work supported under the grant is directed at both the bulk and the thin-film forms of these oxides with the ultimate objective of elucidating the underlying mechanism(s) for the superconductivity of these materials.

The new materials, and the prospect of future discoveries involving ultra-high transition temperature superconductivity have greatly broadened interest in superconductivity in both the Engineering and Scientific Communities. Superconducting materials may be offered as a solution to a variety of problems in areas of technology hitherto abandoned to more conventional materials. The prospect of practical superconductivity at liquid nitrogen temperatures (and perhaps higher) could have an enormous impact on a variety of industrial and military technologies in areas relating to energy, electronics and information processing.

It is clear that future technological success is related to the ability to control the chemical composition and morphology and perhaps with the development of the capability to fabricate thin films of prescribed morphology and chemical composition. Although most of the advances in the limiting values of superconducting parameters have come from empirical discoveries associated with highly Edisonian fabrication efforts, optimization of the properties may result from theoretical modeling which should point the way towards future improvements in such properties. The efforts involved in preparing samples of sufficient quality to test theoretical models and answer other scientific questions are closely related to those efforts needed for the development of materials adequate for superconducting technology.

The history of the past two and a half years of research on high temperature superconductors demonstrates that a major on-going technical challenge in the field, in addition to finding additional materials with even higher T_c's, is the preparation of materials of exceptionally high quality. This would permit intrinsic superconducting properties to be determined with a certain degree of confidence,

thus facilitating the elucidation of the mechanism for high temperature superconductivity.

The complementary skills and backgrounds of the two principal investigators have been applied to solve both fabrication and analytical problems in order to meet the above challenge. Materials have been fabricated in both bulk and thin film form and characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and scanning electron microscopy (SEM). These studies have been correlated with investigations of macroscopic superconducting properties such as critical temperatures, transition widths, critical magnetic fields, the Meissner effect, and penetration depths. Progress in the fabrication of thin films has progressed to the point where the fabrication of planar tunneling junctions and proximity effect structures may actually be feasible in the short term.

In the next section we will describe our progress in the eighteen month period which was completed on 28 February 1989. The subsequent sections will enumerate the personnel involved in the program, and list the publications and reports.

II. PROGRESS

A. Facilities

There have been several efforts relating to facilities development during the first eighteen months. These include work on improvement of the electron beam evaporation system available to the program, the construction of a spherical-target dc sputtering system used in collaboration with an Electrical Engineering colleague, the establishment of a complete laboratory for the fabrication of bulk ceramic samples, and the refinement of our scanning tunneling microscope capabilities. A second version of the multiple source thermal evaporation system has been designed and purchased from the Physical Electronics Division of Perkin Elmer Corporation. Delivery is expected before the end of the calendar year. All new facilities expenditures have been supported by funds supplied by the Central Administration of the University of Minnesota and administered through the Institute of Technology Dean's Office.

The multi-source electron beam deposition system used to prepare high-T_c films was converted successfully from its previous uses involving lanthanum sulfur compounds. An ozone generator and distillation apparatus has been built and installed in this system. The use of this equipment in the preparation of high transition temperature superconducting films will be described below. The acquisition of an entirely new evaporation system, as mentioned above, should result in both an enhancement in the quality of films which can be produced as well as an increase in the rate at which they can be produced.

In collaboration with F. Wehner, of the Electrical Engineering department we have designed a new dc sputtering system with spherical targets (see below). The vacuum chamber was delivered during the summer and currently efforts are under way to make it operational.

Various glove boxes, ovens, and mills have been purchased so that we have a complete facility for the fabrication of bulk ceramic samples. These will be used as sputtering targets and will serve as raw materials for single crystals needed for various investigations.

During the course of the year we became aware of a critically useful analytical capability provided as a service by the Geology Department, Direct-Coupled-Plasma-Atomic Emission Spectroscopy

(DCP-AES). The availability of this accurate tool for chemical analysis has contributed in a singular way to our progress in thin film fabrication over the past year.

B. Fundamental Studies of Bulk High Temperature Superconductors

Investigations of magnetic and electronic properties and Scanning Tunneling Microscope (STM) studies were carried out on bulk and single-crystal samples which were initially available to the program shortly after its inception. The measurements were carried out using a Superconducting Susceptometer, an XPS machine available in the Surface Analysis Center, and a STM in Professor Goldman's laboratory.

The time dependence of the magnetization of both polycrystalline and single-crystal samples of $YBa_2Cu_3O_{7-x}$. was investigated as a function of temperature. and magnetic field[1-3]. The decay rate was found to have a maximum at about 40K. Slow rates of decay were found to persist and to continuously decrease with increasing temperature up to the superconducting transition. These effects were originally thought to be associated with and support the superconducting glass behavior of high temperature compounds first suggested by Muller. An alternative model in which the dynamics is associated with anomalous giant flux creep of vortices has been suggested by the I. B. M. group. These two descriptions may be alternative ways of describing the same phenomenon. An experiment which may perhaps resolve the issue is being prepared in which the decay phenomenon will be studied in a granular Type-I superconductor which does not sustain Abrikosov vortices..

X-ray photoelectron spectroscopy studies (XPS) were performed on bulk polycrystalline samples of $YBa_2Cu_3O_{7-x}$ as a function of temperature through the superconducting transition[4]. With decreasing temperature, clear changes were observed in the photoelectron spectrum which were interpreted as signatures of the Cu^{3+} and perhaps the Cu^{1+} oxidation states, in addition to the usual Cu^{2+} state. These changes were not observed in samples which had been rendered nonsuperconducting by baking in vacuum. Results of this type have been obtained by a number of workers and the precise significance for superconductivity of measurements of this type remains an open question at this time.

Tunneling into the c-axis direction of single crystals of $YBa_2Cu_3O_{7-x}$ was studied using an STM with a tungsten tip apparently in a tunneling rather than in a point contact mode[5]. A wide range of values of voltage that might be associated with the feature in the I-V characteristic usually associated with the energy gap were observed. Subsequent investigations in our laboratory and in other places suggests that most of the effects measured using STM are associated with charge transfer effects at the surface. It is possible to determine the energy gap in a granular superconductor in the presence of such charging effects, but it has not been done to date in a convincing manner with a high temperature superconductor. Quantitative tunneling results will require the development of single crystals or single-crystal films with well-defined surfaces.

C. Thermal Co-evaporation of High-T_c Films

Coevaporation has been used to prepare thin films of the $Y_2Ba_4Cu_8O_{20-x}$ compound using a combination of electron beam and Knudsen vapor sources.[6] the best film exhibited a superconducting onset at 80K and zero resistance at 72K. X-ray diffraction analysis indicated that the films were nearly single phase "248" with a small $YBa_2Cu_3O_{7-x}$ ("123") impurity. This work was the first reported confirmation of the findings of the Stanford group relating to the same material. The crystal structure of our films, in contrast with the reports of the Stanford group was stable when subjected to high temperature annealing. The best film also exhibited a positive rather than a negative zero-temperature intercept in its resistance versus temperature curve which is also in contrast with the large negative intercepts reported by the Stanford group.

The major accomplishment during the first year of the grant was the development of a technique for the in-situ formation of high T_c superconducting films using an ozone vapor jet as an oxygen source[7-9]. Films exhibiting zero resistance at temperatures as high as 89K were fabricated in-situ under high vacuum conditions using substrate temperatures of 700^0C without a post-evaporation anneal in oxygen. This process has implications for in-situ measurements of fully superconducting surfaces using a variety of probes as well as for the fabrication of devices and structures whose properties are dependent on surfaces and interfaces. The fact that superconducting

transition temperatures of 40K were achieved with substrate temperature as low as 590^0C suggests that the method has great promise for the fabrication of high temperature superconducting films on substrates such as Si rather than the more exotic $SrTiO_3$ substrates typically used in such work.

D. Sputter-Deposition of High-T Films

In collaboration with G. K. Wehner and Y. H. Kim of the Electrical Engineering Department we have grown films of both $YBa_2Cu_3O_{7-x}$ and BiSrCaCuO by sputtering from a stoichiometric target of hemispherical shape[10, 11]. Sputtering was carried out using a Hg vapor triode plasma. Films of the "123" compound exhibited transition widths of about 2.5K with zero resistance being achieved at 89K. These films, although epitaxial were not single crystal. Recently films of Tl-Ba-Ca-Cu-O with transition temperatures of greater than 100K were prepared using these same techniques. At the present time efforts at optimizing the process for these materials are under way.

E. Fluctuations and the Superconducting Transition in c-axis Oriented Tl-Ba-Ca-Cu-O Thin Films.

Films of Tl-Ba-Ca-Cu-O prepared by a former member of our group, J. H. Kang, were made available to us by Kenneth Gray of Argonne National Laboratory. Two separate, but related, investigations were carried out using these materials, a study of fluctuation conductivity in the normal state above the superconducting transition, and a study of the transition itself, within the context of the Kosterlitz-Thouless model. The systematics of the superconducting phase transition and the fluctuations above Tc are of interest because of the possible insights into the relationship between the two dimensional organization of the conducting planes and the mechanism for superconductivity in these materials.

Measurements of the in-plane fluctuation enhanced conductivity were performed over the temperature range from T_c to 240K. The results were consistent with two-dimensional fluctuation theory and with a linear dependence of the normal resistivity on temperature down to $(T-T_c)/T_c$ the order of 0.03. A crossover to three-dimensional fluctuations close to T_c was not found. The width of the superconducting transition was actually narrower than what might have

been expected from the elementary theory given by Lawrence and Doniach. It is possible that this is an intrinsic effect not connected with morphology, but associated with the coupling of the CuO_2 layers which is not contained in the phenomenological theory.

The electrical properties of $Tl_2Ba_2CaCu_2O_8$ were also examine within the context of the Kosterlitz-Thouless model. In particular, nonlinear current-voltage and resistivity-magnetic field characteristics were studied below the Kosterlitz-Thouless temperature, T_c. Within the context of the Kosterlitz-Thouless model of the superconducting transition, these were found to be consistent with each other and with the exponential inverse square root temperature dependence of the resistivity just above T_c. The parameterization of the resistivity data well above the transition by the Aslamazov-Larkin theory of superconducting fluctuations, as discussed above was also found to be consistent with that of the Kosterlitz-Thouless model.

These results appear to b e consistent with a picture of the transition in which there is no measurable effect of the coupling between layers. Films which are geometrically three dimensional in character can behave as if they are two dimensional only if the effect of interlayer coupling is unimportant.

F. Sol-Gel Processing of High-T_c Films

Alkoxide based systems were investigated for their suitability for sol-gel coatings[14]. The sol-gel process involves forming a solution which is later pyrolyzed in order to generate the oxide. Coatings can be easily made by dip coating or spin coating the solution unto substrates. The best results were obtained with 2-ethoxyethanol solutions of $Y(O\text{-}i\text{-}Pr)_3$, $Ba(OCH_2CH_2OEt)_2$, and $Cu(acac)_2$. Difficulties encountered included the requirement of multiple coatings to build up the thickness (each coating only a few hundred Angstroms thick), diffusion of cations from the substrate into the thin films, cracking of the films upon drying and pyrolyzing, poor adhesion of films to substrates, nucleation of separate crystals with random orientations instead of epitaxial growth, and impurity phase formation. However, by searching through the appropriate parameter space, $YBa_2Cu_3O_{7-x}$ thin films (approximately 3500Å thick) with structural integrity and good adhesion to the substrate (single crystal strontium titanate) were fabricated with a T_c of 80K[15]

F. Microstructural Characterization

Transmission electron microscopy (TEM) studies provided critical information on the defect structure of the thin films fabricated by various processing routes. Almost perfect epitaxy was found for films grown in situ by the new ozone processing with a substrate temperature of 700° C, while low substrate temperatures of 590°C produced films with small misorientations and a lower Tc[16,17]. Twins were rarely observed in thin films, but defects which included extra Cu-O planes were predominant in many types of thin film samples (identified by large lattice spacings of 12-14Å).

Auger, XPS, and Energy Dispersive Spectroscopy (EDS) were investigated for their suitability to determine the chemical compositions of thin films and bulk materials. Standards were established for using EDS in the SEM to determine the exact chemical composition of oxide superconductors. (Unfortunately, this technique would not work if thin films were deposited on $SrTiO_3$ substrates due to the overlap of the Ba and Ti peaks). Auger and XPS were difficult to quantify, and mainly measured only the composition of the top few surface layers of the samples.

II. PERSONNEL

A. Fabrication of Thin Films and Fundamental Physical Studies

A. M. Goldman, Professor of Physics
B. Johnson, Research Associate in Physics
D. Berkley, Research Assistant in Physics
T. Wang, Research Assistant in Physics
D. H. Kim, Research Assistant in Physics and Graduate School Fellow
M. Tuominen, Research Assistant in Physics
Y.. Kim, Research Assistant in Electrical Engineering
G. Wehner, Emeritus Professor of Electrical Engineering
L. Conroy, Associate Professor of Chemistry (deceased)

B. Characterization of Thin Films

M. Mecartney, Assistant Professor of Chemical Engineering and Materials Science
K. Beauchamp, Research Assistant in Materials Science
Y. J. Zhang, Research Associate in Materials Science
Loren Eyres, Undergraduate in Electrical Engineering
Eric Montei, Summer researcher, Undergraduate in Physics, Gustavus Adolphus College

C. Thin Films by Sol-Gel Processing

M. Mecartney, Assistant Professor of Chemical Engineering and Materials Science
Wayne Gladfelter, Associate Professor Chemistry
Beth Hassler, Graduate Student in Materials Science
Marquita Accibal, Graduate Student in Chemistry
Allen Gabor, Undergraduate in Materials Science

Support for the undergraduate researchers was provided in part by the NSF Summer Undergraduate Research Program in the Department of Chemical Engineering and Materials Science, and by the Undergraduate Research Opportunity Program at the University of Minnesota. W. Gladfelter, L. Conroy, G. Wehner, Y. Kim, D-H. Kim, and M. Tuominen, B.Hassler and M.Accibal drew no salaries from the AFOSR program. Dr. Zhang is half-time on this project.

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9. "Techniques for the Growth of Superconducting Oxide Thin Films Using Pure Ozone Vapor," D. D. Berkley, A. M, Goldman, B. R. Johnson,

J. Morton, and T. Wang, submitted to Review of Scientific Instruments.

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12. "Fluctuation conductivity of Tl-Ba-Ca-Cu-O thin films," D. H. Kim, A. M. Goldman, J. H. Kang, K. E. Gray, and R. T.Kampwirth, Physical Review B39, 12275 (1989).

13. "Kosterlitz-Thouless Transition in $Tl_2Ba_2CaCu_2O_8$ Thin Films," D. H. Kim, A. M. Goldman, J. H. Kang, and R. T. Kampwirth, submitted to Physical Review B.

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16. "Microstructural Analyses of $YBa_2Cu_3O_{7-x}$ Superconducting Thin Films Grown in Situ by Ozone Processing," Y. J. Zhang, M.L. Mecartney, D.D. Berkeley, B.R. Johnson, and A.M. Goldman. Manuscript in preparation for submission to Journal of Materials Research.

17. "The Structure of Epitaxial Superconducting Oxide Films Grown by Ozone Processing," Y. J. Zhang, M.L. Mecartney, D.D. Berkeley, B.R. Johnson, and A.M. Goldman. Presented at the Spring MRS 1989 Meeting.